

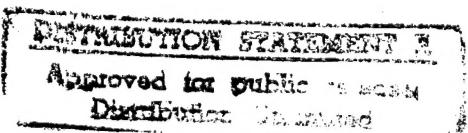
EFFECTS OF SPECIATION IN SEDIMENT-WATER EXCHANGE OF METALS
(ONR GRANT N00014-93-1-0899)

PROGRESS REPORT: 15 JUNE 1993-15 JUNE 1994

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<p>Beginning in October 1993, we sampled sediments from two estuarine sites in Chesapeake Bay having contrasting biogeochemical and physical characteristics. Temporal variability at these sites has been examined during fall '93 and spring '94. Our results show that total dissolved copper concentrations in upper pore water intervals (8-11 nM) are similar to bottom water concentrations (5-12 nM). Virtually all of the copper (96.9 to 99.9%) dissolved in the pore waters and bottom waters of these two sites exists in electrochemically non-labile forms, probably as organic or mixed organic-inorganic (e.g., sulfide-containing) complexes. Such forms generally are regarded as being unavailable for biological uptake. The most striking result is that concentrations of copper-binding ligands in the upper intervals of the pore waters are at least 10 times greater than in the bottom waters. Despite similar levels of DOC in the pore waters at the mid-Bay site (site M) and at the lower Bay site (site S), levels of copper-binding ligands are 2 to 3 times greater in the pore waters at site M than at site S. In addition, the concentration gradient of copper-binding ligands across the sediment-water interface is much larger at site M than at site S, suggesting the stronger possibility of a benthic flux of such ligands from site M sediments. These differences may result from the dissimilar physical and chemical characteristics of the two sites. These results will guide our second- and third-year goal of quantifying fluxes of dissolved copper and copper-binding ligands across the sediment-water interface in Chesapeake Bay and the adjacent coastal Atlantic shelf/slope region.</p>			
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**EFFECTS OF SPECIATION IN SEDIMENT-WATER EXCHANGE OF METALS
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The goal of our studies are to examine the effects of chemical speciation on the fluxes of dissolved copper across the sediment-water interface. Beginning in October 1993, we sampled the sediments (by box corer) from two estuarine sites in Chesapeake Bay (sites M and S) having contrasting biogeochemical and physical characteristics. So far, temporal variability at these sites has been examined during two seasons (fall and spring).

Site M is in the mesohaline portion of Chesapeake Bay where seasonal anoxia or low oxygen conditions generally occur during the summer months (see map in Burdige and Homstead, 1994). The sediments at this site are organic-rich and sulfidic, with sulfate reduction (and to a lesser extent methanogenesis) being the predominant organic carbon remineralization processes. The sediments are devoid of benthic macrofauna, except in spring when there is limited colonization of the sediments by small polychaetes and molluscs (Kemp *et al.*, 1990).

Site S is in the southern Chesapeake Bay and has a well-characterized benthic community, with large tubes and burrows (Schaffner, 1990). Extensive bioturbation in these sediments can be seen both visually and by lack of significant pore water and solid phase gradients (Burdige and Homstead, 1994). Although Marvin and Capone (1992) report that integrated annual rates of sulfate reduction at site S are half those of the more organic-rich site M sediments, virtually all sulfide produced by this process at site S is re-oxidized (Burdige and Homstead, 1994), presumably as a result of macrofaunal activity either transporting oxygen (Berner, 1980; Aller, 1982) or downwardly mixing solid phase Mn oxides (Aller and Rude, 1982) into the sediments.

We processed all cores under N_2 to minimize oxidation artifacts in suboxic and anoxic sediments. Pore waters were extracted from sediments by centrifugation at *in situ* temperatures. Trace metal-clean techniques were employed throughout sample processing and analysis. Concentrations of total dissolved Cu (TDCu: 0.4 μm -filtered) and Cu-binding ligands were determined, along with dissolved organic carbon (DOC), Fe, Mn, sulfide, nutrients, and ΣCO_2 . Bottom water and pore water samples were titrated with copper, and the titrations were monitored using differential pulse anodic stripping voltammetry on both hanging mercury drop and thin mercury film rotating glassy carbon disk electrode systems.

Our results to date show that overall concentrations of total dissolved copper in upper intervals of the pore waters (8-11 nM) are generally similar to bottom water concentrations (5-12 nM). Virtually all of the copper (96.9 to 99.9 %) dissolved in the pore waters and bottom waters of these two Chesapeake Bay sites exists in electrochemically non-labile forms, probably as organic or mixed organic-inorganic (e.g., sulfide-containing) complexes. Such forms generally

are regarded as being unavailable for biological uptake.

The most striking result we encountered is that concentrations of copper-binding ligands in the upper intervals of the pore waters are at least 10 times greater than in the bottom waters. Despite similar levels of DOC in the pore waters at the mid-Bay site (site M) and at the lower Bay site (site S), levels of copper-binding ligands are 2 to 3 times greater in the pore waters at site M than at site S. In addition, the concentration gradient of copper-binding ligands across the sediment-water interface is much larger at site M than at site S, suggesting the stronger possibility of a benthic flux of such ligands from site M sediments. These differences may result from the dissimilar physical and chemical characteristics of the two sites.

These results will guide our second- and third-year goal of quantifying fluxes of dissolved copper and copper-binding ligands across the sediment-water interface in Chesapeake Bay and the adjacent coastal Atlantic shelf/slope region.

REFERENCES

Aller, R.C. 1982. in Animal-sediment relations, The biogenic alteration of sediments. (P. L. McCall and M. J. S. Tevesz, ed.). pp. 53-102. Plenum Press.

Aller, R.C. and P.D. Rude. 1982. Geochim. Cosmochim. Acta 52:751-765.

Berner, R.A. 1980. Early Diagenesis, A Theoretical Approach. Princeton University Press.

Burdige, D.J. and J. Homstead. 1994. Geochim. Cosmochim. Acta 58: 3407-3424.

Kemp, W.M., et al. 1990. Limnol. Oceanogr. 35:1545-1563.

Marvin, M.C. and D.G. Capone. 1992. Abstract presented at the 1992 ASLO Aquatic Sciences meeting.

Schaffner, L.C. 1990. Mar. Ecol. Prog. Ser. 61:107-117.